

Structure and Magnetization of Co₄N Thin Film

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Abstract

In this work, we studied the local structure and the magnetization of Co₄N thin films deposited by a reactive dc magnetron sputtering process. The interstitial incorporation of N atoms in a fcc Co lattice is expected to expand the structure and such expansion yields interesting magnetic properties characterized by a larger than Co magnetic moment and a very high value of spin polarization ratio in Co₄N. By optimizing the growth conditions, we prepared Co₄N film having lattice parameter close to its theoretically predicted value. The N concentration was measured using secondary ion mass spectroscopy. Detailed magnetization measurements using bulk magnetization method and polarized neutron reflectivity confirm that the magnetic moment of Co in Co₄N is higher than that of Co.

Keywords: Co₄N thin films, reactive sputtering, Magnetization

1. Introduction

Transition metal nitrides (TMN) are an interesting class of compounds as N incorporation in metals make them less corrosive and results in interesting properties such as superhardness [1, 2, 3, 4], superconductivity [5], corrosion and wear resistance [6, 7]. In particular, tetra metal nitrides M₄N, generally formed only for late 3d TM (e.g. Fe, Co, Ni) [8] are somewhat unique in the sense that they share a common fcc structure. Due to a dominant metal-metal interactions in M₄N they possess metal like character (unlike metal oxides) [9]. In a metal fcc cage, the incorporation of N atoms at the interstitial positions, results in an expansion of the unit cell, which in turn affects the magnetic integrations [10, 11, 12, 13, 14]. Generally incorporation of a non-magnetic element in a magnetic one is expected to result in a loss of magnetic moment (M) explained by the well-known Slater-Pauling curve [9]. However, theoretical calculations predict M to be larger for Fe₄N and Co₄N compounds. This is an interesting proposition as with larger than metal M , corrosion resistance and a metal like character can make M₄N compounds an alternative their pure metal counterparts. In addition, some recent theoretical predicted a very spin polarization ratio (SPR) for M₄N compounds [10, 11]. Among them Co₄N is predicted to have SPR \sim 90% [11] which is among the highest values for any compound.

However experimental results obtained so far for Co₄N compounds does not seems to be as exciting as theoretical calculations. This can be understood from the fact that the value

of M found in most of the experimental works so far is perpetually less than that of pure Co. A closer look at the Co₄N thin films reveal that the values of lattice parameter (LP) obtained in most of the experimental works is typically 3.54 Å [15, 16, 17, 18, 19, 20, 21]. This is more close to theoretical values LP for fcc Co at 3.54 Å than that of Co₄N at 3.72 Å [10, 11, 15]. Such a discrepancy in the experimental and theoretical values of LP for Co₄N requires attention. While investigating the recipes adopted for formation of Co₄N thin films, we found that Co₄N films were often deposited at substrate temperatures (T_s) similar to those used for Fe₄N thin films. This is convenient approach due to similarity between the Fe₄N and Co₄N and the absence of a phase diagram for the system Co-N, intuitively makes one to follow paths adopted for preparation of Fe₄N.

However, the energetics of nitride formation for Fe₄N and Co₄N immediately indicates about the complexity for the later. Theoretical values of enthalpy of formation (ΔH_f°) for Fe₄N is about -12 kJ mol⁻¹ [22], whereas those for Co₄N are slightly above or below 0 for hcp Co or fcc Co [11]. This also implies that at a higher T_s , Co₄N system will be less stable as compared to Fe₄N. In a recent work, we studied the phase formation process in the Co-N system at $T_s = 300$ K [23] and 523 K [24]. We found that at $T_s = 523$ K, N incorporation in the Co-N system is minimal and the phases formed are similar to a fcc Co having LP \sim 3.52 Å. On the other hand when T_s is lowered to 300 K Co-N depicts a similar type of phase formation sequence as found for the Fe-N system [25, 26]. By optimizing the deposition

conditions, Co_4N film having LP as high as 3.68 \AA can be deposited and the value of M also supersedes that of Co. Since the Co_4N films deposited without any intentional heating are expected to have a large fraction of disorder, estimation of LP with x-ray diffraction alone may not be decisive, therefore in the present work, we investigate the local structure and M of the Co_4N thin film deposited at $T_s = 300 \text{ K}$ using x-ray absorption based techniques. By doing measurements at Co K and L-edges and at N K-edge, we get valuable information about the local structure. In addition, by doing polarizer neutron reflectivity (PNR) measurements at low temperatures ($\sim 20 \text{ K}$) we determined the value of M for Co_4N thin film. Obtained results are presented and discussed in this work.

2. Experimental

We deposited Co_4N thin film with a nominal thickness of 120 nm at $T_s = 300 \text{ K}$ (without intentional heating) using a reactive direct current magnetron sputtering (dcMS) system (Orion-8, AJA Int. Inc.). A one inch diameter and 0.5 mm thick pure Co (purity 99.95%) target was sputtered using a gas mixture of Ar and N_2 (both 99.9995% pure) gases. With a base pressure of $1 \times 10^{-7} \text{ Torr}$, the pressure during deposition was about 3 mTorr . More details about deposition process can be found in [23]. Along with the Co_4N sample, we also deposited a pure Co thin film under identical conditions as a reference.

To investigate the local and electronic structure, x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure measurements (EXAFS) were performed in the total electron yield (TEY) and fluorescence mode at BL-01 [27] and BL-09 beamlines, respectively at the Indus-2 synchrotron radiation source at RRCAT, Indore. The measurements in TEY mode at BL-01 were carried out in a UHV chamber with a base pressure of $(2 \times 10^{-10} \text{ Torr})$. To avoid surface contaminations, samples were cleaned *in-situ* using a Ar^+ source kept incident at an angle of 45° . The measurement in fluorescence mode at BL-09 were carried out at ambient conditions.

The composition of Co_4N thin film was measured using secondary ion mass spectroscopy (SIMS) depth profiling using a Hiden Analytical SIMS workstation. An oxygen ion beam of energy 4 keV and 200 nA was used as a primary source and the sputtered species were detected using a quadrupole mass analyzer. The SIMS depth profiles were compared with a reference sample as described in [23]. The magnetization measurements were carried out using a Quantum Design SQUID-VSM (S-VSM) magnetometer at room temperature. We did PNR measurements at AMOR reflectometer [28] in the time of flight mode at SINQ-PSI Switzerland. To saturate the sample magnetically, a magnetic field of 0.5 T was applied during the PNR measurements. The measurements at low temperature were carried out using a close cycle refrigerator installed inside the electro magnet.

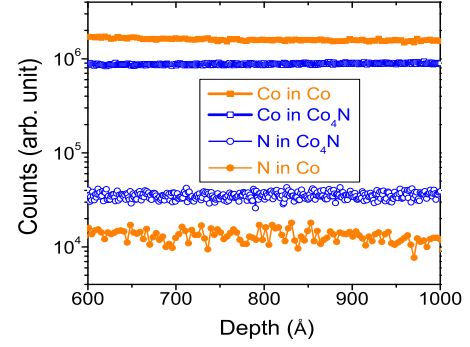


Figure 1: (Color online) SIMS depth profiles of Co and Co_4N thin films samples.

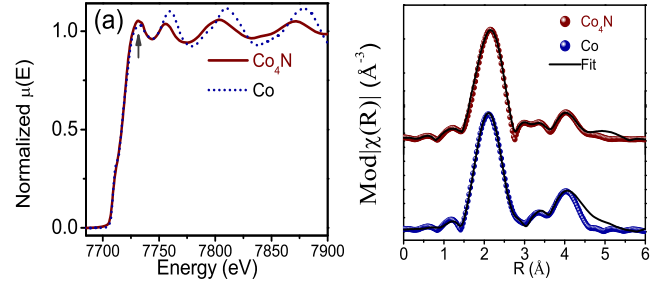


Figure 2: (Color online) Normalized Co K-edge XANES spectra of Co_4N and Co foil samples (a). Fitted k^2 weighted spectra for Co_4N and a Co samples (b).

3. Results and Discussion

To quantify the N at.% in our samples, we did SIMS depth profiling measurements. The SIMS depth profiles for the Co_4N sample are shown in fig. 1 along with a Co reference sample. The depth profiles clearly reveal that N concentration in the Co_4N sample is more and the Co concentration is less as compared to Co sample. Following a procedure described in ref. [23] and measuring a reference sample with known concentration, we found that N at.% comes out to be $\sim 18(\pm 2)\text{at.}\%$ indicating formation of Co_4N phase.

X-ray diffraction measurements (not shown) carried out in our samples resulted in similar patterns as observed in a earlier work [23]. Since samples are deposited without any intentional heating, the long range structure is expected to somewhat disordered and more reliable information about the structure can be obtained from a local probe like x-ray absorption spec-

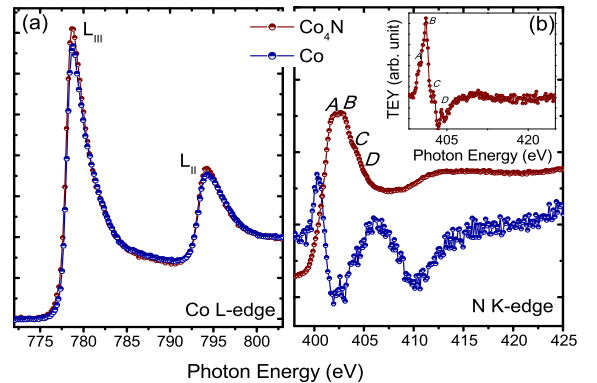


Figure 3: (Color online) XAS spectra of Co_4N and Co thin film at Co-L-edge (a) at N K-edge (b). The inset in (b) shows the derivative of N K-edge in Co_4N .

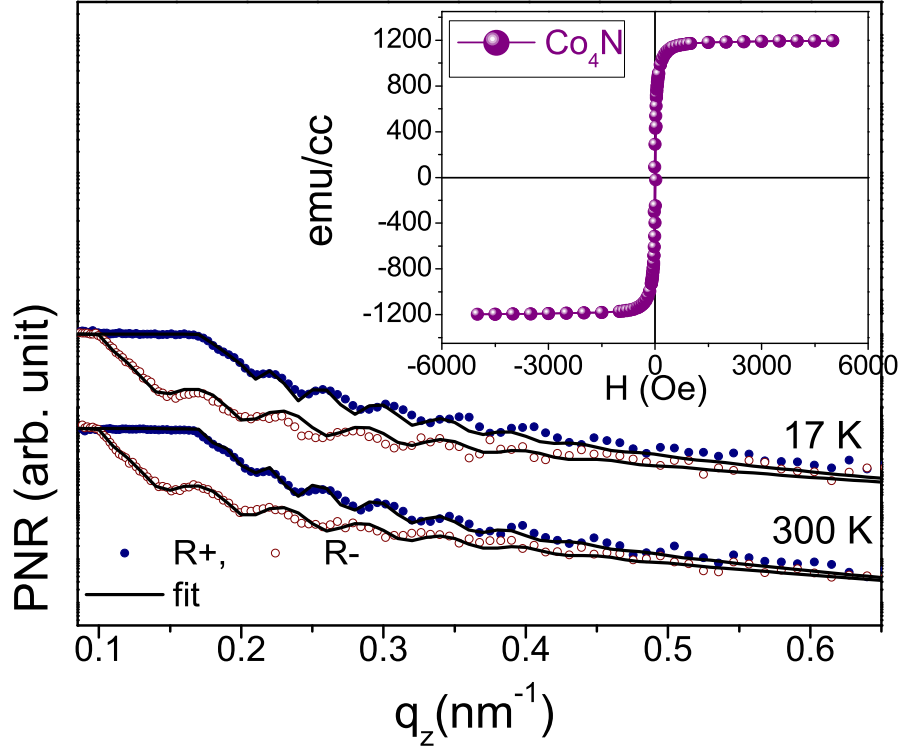


Figure 4: (Color online) (a). PNR patterns of Co_4N thin film taken at room temperature and 17 K. Inset showing the M-H curve at room temperature of Co_4N .

troscopy. To get complementary information, we did XANES measurements at Co K and L-edges and at the N K-edge. In addition, EXAFS measurements were also carried out at Co K-edge. Fig. 2(a) and (b) shows the normalized XANES and EXAFS patterns for Co_4N sample together with a Co metal as a reference. It can be clearly seen that the intensity in the white line region is higher in the Co_4N sample (marked by an arrow in 2(a)), which essentially arises due to hybridization between face centered Co 3d and N 2p bands through σ^* anti-bonding and an enhancement in density of states in Co_4N as compared to Co. Such effects are even more pronounced at Co L-edges as shown in fig. 3(a). Here presence of N in Co_4N thin film can also be confirmed by comparing the N K-edge spectrum of Co_4N with that of a Co reference sample as shown in fig. 3(b). The features in N K-edge spectra are labelled as A, B and C. Here the feature A is attributed to a dipole transition from N 1s to hybridized states of face centered Co 3d and N 2p orbitals through π^* anti-bonding. Features B and C represents the dipole transition from N 1s to hybridized states of face centered Co 3d and N 2p orbitals through σ^* anti-bonding [29, 30]. These results obtained from XAS measurements provide a strong evidence for the Co_4N structure.

Further information about the LP can be obtained from EXAFS measurements. Fig. 2(b) shows the moduli of k^2 weighted EXAFS data for Co_4N and with a Co reference. For Co_4N structure we consider space group $Pm\bar{3}m$ and $\text{LP} = 3.74 \text{ \AA}$. Among other parameters the fitting of EXAFS data also yields the distance between corner Co atoms which is equal to the LP. We found that the LP comes out to be 3.92 \AA with ($\sigma^2 = 0.0145 \text{ \AA}^2$); these values for the Co reference sample are 3.47 \AA with ($\sigma^2 = 0.0093 \text{ \AA}^2$). The value of LP obtained in our case is considerably larger than that of Silva *et.al.* [15]

in a recent work for their Co_4N thin film. They found $\text{LP} = 3.53 \text{ \AA}$ with ($\sigma^2 = 0.005 \text{ \AA}^2$). Considering even large inaccuracy of EXAFS technique in determination of LP, our values are considerably larger and clearly indicate an expansion in the Co lattice by incorporation of N. It may be noted that Silva *et.al.* [15] deposited their samples at a $T_s = 523 \text{ K}$ and at this temperature it may happen that most of N atoms diffuse out of the system leaving behind a dominant fcc Co as found in our recent work [24].

It may be noted that in most of experimental work carried out in the Co_4N thin films always a high T_s was used and the measured values of LP were closer to fcc Co rather than that of Co_4N . Since LP and the M are correlated and an expansion in the LP due to interstitial incorporation of N atoms is responsible for enhanced M [11], the values of M obtained in most of the works were closer to pure Co. To measure M in our samples we did bulk magnetization and PNR measurements. Inset of fig. 4 shows M-H loop measured using S-VSM at room temperature for a Co_4N thin film. We find that $M = 1195 \text{ emu/cc}$ which approximately corresponds $1.6\mu_B$ per Co atom, which is slightly lower than the theoretically predicted value of M for Co_4N . Exact determination of M from bulk magnetization measurements in a thin film sample require precise values of sample volume and density. While the former can be measured with a great accuracy, estimation of later is not easy due to relatively large fraction of defects etc. in thin films. In addition diamagnetism of substrate always interferes with sample magnetization.

It is well-known that in a PNR measurement, absolute value of M can be measured as in PNR technique, measurement of M is not influenced by sample volume and substrate magnetism. On the other hand density of the film is inherently measured in PNR. In this context it is surprising to note that PNR has not

been used to measure M in Co_4N thin films. In most of the works available so far, M was measured using bulk magnetization methods and there seems to be a large variations in estimation of M for Co_4N thin films ranging from 1.3 to $1.6\mu_{\text{B}}/\text{atom}$ [17, 19, 20, 21, 29].

We performed PNR measurement at room temperature and at 17 K (to minimize thermal fluctuations) under an applied magnetic field of 0.5 T, which is sufficient to saturate sample magnetically (see inset of 4). The spin-up down reflectivities clearly show a separation typically expected for a ferromagnetic sample. The fitting of PNR patterns was carried out using SimulReflec programme [31] and the obtained values of M are $1.73(\pm 0.05)\mu_{\text{B}}/\text{atom}$ at 300 K and $1.75(\pm 0.05)\mu_{\text{B}}/\text{atom}$ at 17 K. This clearly shows that M is larger than Co in Co_4N thin film. Though such enhancement in M was theoretically predicted, it has been unambiguously demonstrated in this work.

4. Conclusion

In conclusion, by measuring the local structure and a we found that LP of Co_4N thin films far exceeds that of previous works and is more closer to its theoretical value. For Co_4N thin films an enhancement in M was expected. By doing precise magnetization measurements using PNR we found enhancement in the Co magnetic moment. In addition, our SIMS depth profile measurements clearly reveal the formation of Co_4N phase and N K-edge measurements further confirms the formation of Co_4N phase.

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